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A Polarographic Investigation of Elemental Sulfur in Kansas Crude Oils

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A POLAROGRAPHIC INVESTIGATION OF ELEMENTAL SULFUR IN KANSAS CRUDE OILS

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INTRODUCTION

The question as to whether crude oil contains elemental or free sulfur has never been definitely settled, although there are many references in the literature to the presence of elemental sulfur in distillates and as condensed crystals in distillation equipment. There are also many references which indicate that a sulfur-bearing crude oil is very likely to evolve hydrogen sulfide during distillation. Inasmuch as distillation is one of the basic tools in separating the components of petroleum, it is helpful in knowing the sulfur content.

The corrosiveness of elemental sulfur to automobile engine parts is well known, and a great deal of care is exercised by petroleum refineries to minimize free sulfur in their products. Therefore, in doctor sweetening careful control of free sulfur addition must be maintained to avoid production of a corrosive gasoline.

The polarographic method of analysis was chosen because of its rapidity (about 20 minutes per sample), sensitivity and accuracy. Elemental sulfur was determined in ten crude oils by a polarographic method which is believed to be accurate and to respond correctly to the presence of sulfur in the oil. The data obtained should prove very helpful in studies of the reactions of sulfur-containing crude oils and explain, in part at least, the evolution of hydrogen sulfide in distillation.

THEORETICAL PRINCIPLES

Publications on polarographic analysis did not begin to appear in American journals until 1937, at which time the subject had already enjoyed 15 years of active growth in Europe and about 300 papers pertaining to it had been published in foreign periodicals, including the well known monograph by Heyrovsky, the originator of polarography. The first monograph in English did not make its appearance until 1941. The present well-established status of polarography is demonstrated by the numerous papers appearing in the literature in the field of analytical chemistry.

If in the presence of a reducible ion, the voltage applied to an electrolytic cell is gradually increased and the corresponding currents are measured, no appreciable current will flow until the decomposition potential of the electrolyte is reached. Until this potential is exceeded, no ions can be deposited and no exchange of electrons between the electrodes and electrolyte can take place. As the applied voltage is increased beyond the decomposition potential, the current will increase rapidly and indefinitely. The current actually shows a slight rise before the decomposition potential is exceeded. There is no satisfactory explanation for this effect which is known as the residual current.

The current finally reaches a limit because the region around the small electrode, which is the cathode, becomes depleted of reducible ions. The only way reducible ions can get into the region around this

electrode is by diffusion from the bulk of the solution. From the laws governing the conditions of diffusion at a dropping mercury electrode and the nature of the growth of the mercury drop, the Ilkovic equation has been derived to express the current at any given time, t, during the life of a drop(19).

$$i_d = 706\ n\ D^{\frac{1}{2}}\ C\ m^{2/3}\ t^{1/6} \text{ microamperes}$$

The term 706 is a combination of numerical constants, arising from the geometric characteristics of the dropping electrode and the electricity required per mole of electrode reaction; n is the number of electrons involved in the reaction; D the diffusion coefficient in cm^2sec^{-1}; C the concentration in millimoles per liter of electroactive material; and m the weight of mercury in milligrams flowing from the capillary per second.

If one electrode, the anode, is made large in area and the current flowing through the electrolytic cell is very small, polarization at this electrode will be negligible. The anode potential will remain constant, and the anode can be used as a reference electrode. If the other electrode, the cathode, is made very small, the polarization of this electrode would approach a maximum and variations in the e.m.f. of the cell would be due almost entirely to changes in the potential of this electrode. Consequently, the microelectrode, as this small electrode is called, can function as an indicator electrode to measure changes in potential while current is flowing. The current through the bulk of the solution is carried by the movement of all of the ions present, but only

ions reducible or oxidizable at the microelectrode can undergo electron exchange and carry the current to the microelectrode.

A typical current-voltage curve, or polarogram, is illustrated in Figure 1. The midpoint of the curve represents the characteristic potential of the particular oxidation-reduction system it represents.k

The half-wave potential, designated by $E_{\frac{1}{2}}$, is defined as the potential of the microelectrode at the midpoint of the polarographic wave with respect to a standard reference electrode-that is, when one half of all the oxidant which reaches the electrode during a finite time is reduced to the corresponding reductant. Being independent of the concentration of electroactive material, half-wave potentials can sometimes serve for the qualitative identification of an unknown material. This is seldom done, since the close proximity of the many different half-wave potentials precludes any identification unless the number of possibilities is strictly limited by the character of the unknown.

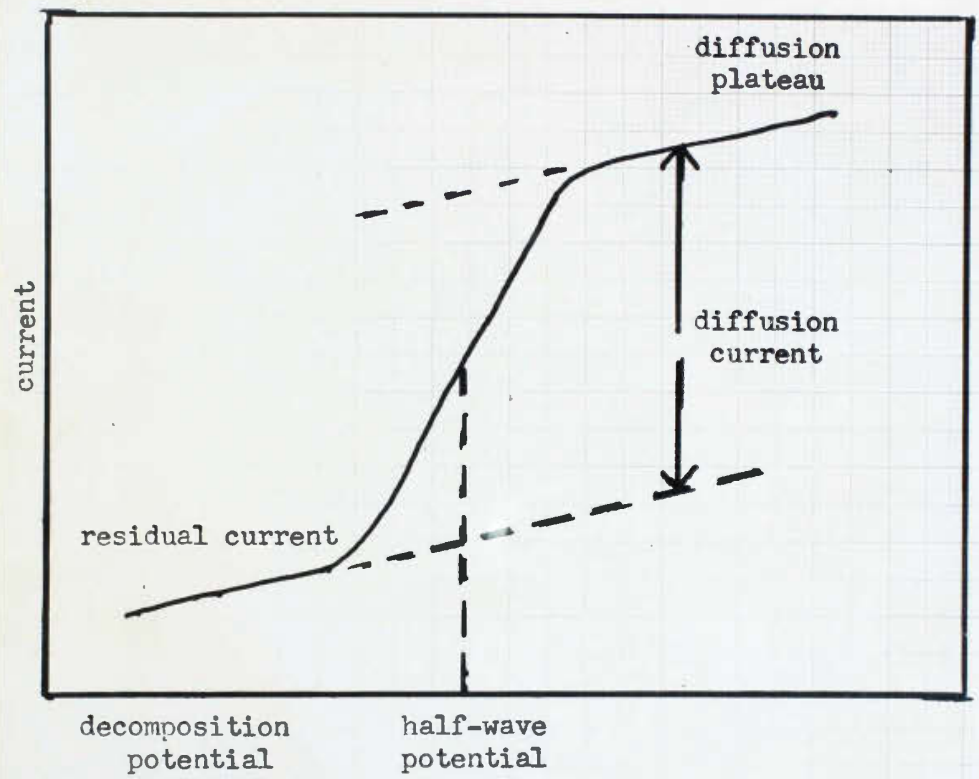

FIGURE 1
Cathodic Polarogram

Current-voltage curves obtained with the dropping mercury electrode are frequently distorted by maxima unless measures are taken to prevent their occurrence. These maxima vary in shape from sharp peaks to rounded humps, which gradually decrease to the normal diffusion current plateau as the applied potential is increased. A rigid explanation of maxima is lacking, although some investigators believe the stirring effect of the growing drop to be responsible; others believe it due to adsorption of electroactive material on the electrode surface. Maxima can usually be suppressed by surface active agents such as dye ions or colloids.

A simple circuit of polarography is shown in Figure 2.

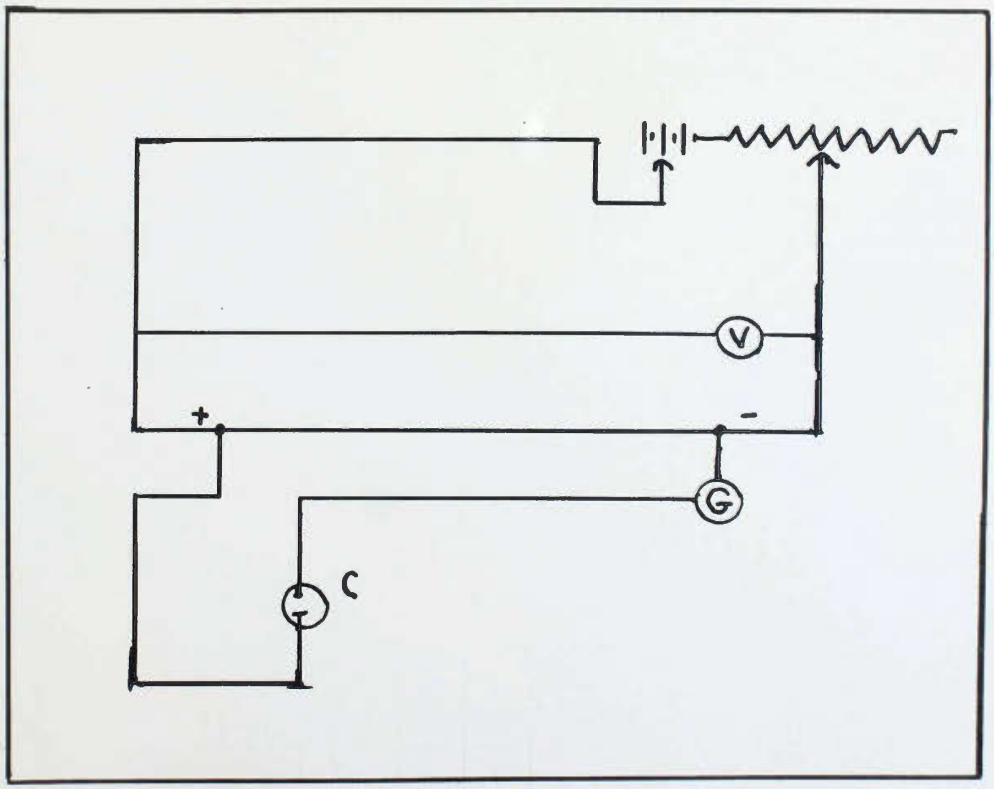

FIGURE 2
Simple Circuit of Polarography

It consists of an accurate slide wire through which the steady current passes. The potential drop across the slide wire is adjusted to any desired value which is read on the voltmeter, V, by inserting one, two, or three dry cells in series and regulating the voltage by means of a series resistance, R. The slide wire contact is moved to vary the voltage applied to the two electrodes. At each voltage setting the current passing through the electrolytic cell C is measured by a suitable galvanometer, G, (19).

Although there are many types of indicator electrodes that can be used in polarographic analysis, the one most widely used is the dropping mercury electrode. This electrode has these advantages: (a) Its surface area is reproducible; (b) the electrode surface is smooth and continually being renewed; (c) mercury amalgamates with many metals and thereby lowers their decomposition potential; (d) hydrogen overvoltage is highest on mercury, enabling work to be done at quite high values of applied voltages without interference from the evolution of hydrogen; and (e) the current assumes a steady value and is reproducible (19).

For a more complete report on theory see Lingane (11, 12, 13, 14, 15), Kolthoff (6, 7, 8, 9, 10), Muller (16, 17), and Daniels (1).

Organic Polarography

Although sulfur is inorganic in nature, crude oil may be considered as being organic; therefore, the general characteristics of organic compounds will be considered here.

In studies of the reduction of organic compounds it is desirable to work with buffer solutions. Frequently the pH of the medium has a great effect upon the half-wave potential since hydrogen ions often participate in the electrode reaction. Consequently, in an unbuffered solution the pH at the electrode surface changes considerably and this causes the waves to be drawn out or sometimes the appearance of two waves (6).

The effect of the medium upon the half-wave potential is a very important one. The insolubility of organic compounds in water makes it necessary that their reduction and oxidation be studied in organic solvents. A mixture of methanol and benzene is fairly suitable since this combination not only dissolves many water-insoluble organic substances and some inorganic salts but also has a reasonable resistance (6).

There is still another effect which has to be considered when dealing with irreversible reductions. Frequently, the half-wave potentials are shifted to more positive potentials and the wave height is decreased by the addition of multivalent cations. The shift of half-wave potentials to more negative values with an increase in pH in acid solution sometimes can be interpreted as a direct reaction of the compound with a proton to form an intermediate ion which is more easily reduced (6).

Elemental Sulfur

According to Proske (18) elemental sulfur produces a cathodic

wave at -0.7v. vs. the saturated calomel electrode in a medium composed mainly of pyridine with sodium acetate and acetic acid as supporting electrolyte. The electrode reaction is the reduction of elemental sulfur to hydrogen sulfide:

$$S + 2H^{+} + 2e \rightleftharpoons H_2S$$

Using xylose as a maximum suppressor Proske found that the diffusion current is directly proportional to the sulfur concentration up to at least seven millimolar, and he applied the wave to the determination of free sulfur in rubber after pyridine extraction.

Hall (4) independently studied the polarographic reduction of free sulfur in a solvent composed mainly of methanol buffered to an apparent pH of 6 with pyridine and pyridinium hydrochloride (90 ml. methanol, 9.5 ml. of pyridine, and 0.5 ml. of concentrated hydrochloric acid). In this medium the half-wave potential is -0.5v. vs. the aqueous saturated calomel electrode.

Hall states (5):

> The effect of pH on the reduction of elemental sulfur are pronounced and the use of buffered solutions for the analysis of elemental sulfur is necessary. A pH of about 5 or 6 has been found to be satisfactory. The higher the pH of the medium, the more negative the half-wave potential becomes, and in neutral and basic solutions the reduction wave for sulfur is not satisfactory for quantitative measurement.

This effect of pH is illustrated in Figure 3 of this paper as was taken from Hall (5). It can readily be seen that on increasing the pH distorts the wave and also makes it more negative.

Diphenyl disulfide can interfere in the analysis of elemental

sulfur since it reduces at about the same voltage as sulfur. The reduction waves of sulfur and diphenyl disulfide can be separated by using a basic medium, but the sulfur wave obtained is not very satisfactory for quantitative analysis (5). Gerber (3) suggested that the combined diffusion current be obtained for sulfur and diphenyl disulfide, that the sulfur be removed with mercury, that the remaining current be measured, and that the sulfur be determined from the difference in the two diffusion current values.

In the preparation of this paper the limitations encountered were limited time and a suitable storage place for the crude oil samples. On standing at room temperature, crude oil sours and sulfur concentration is believed to increase with souring.

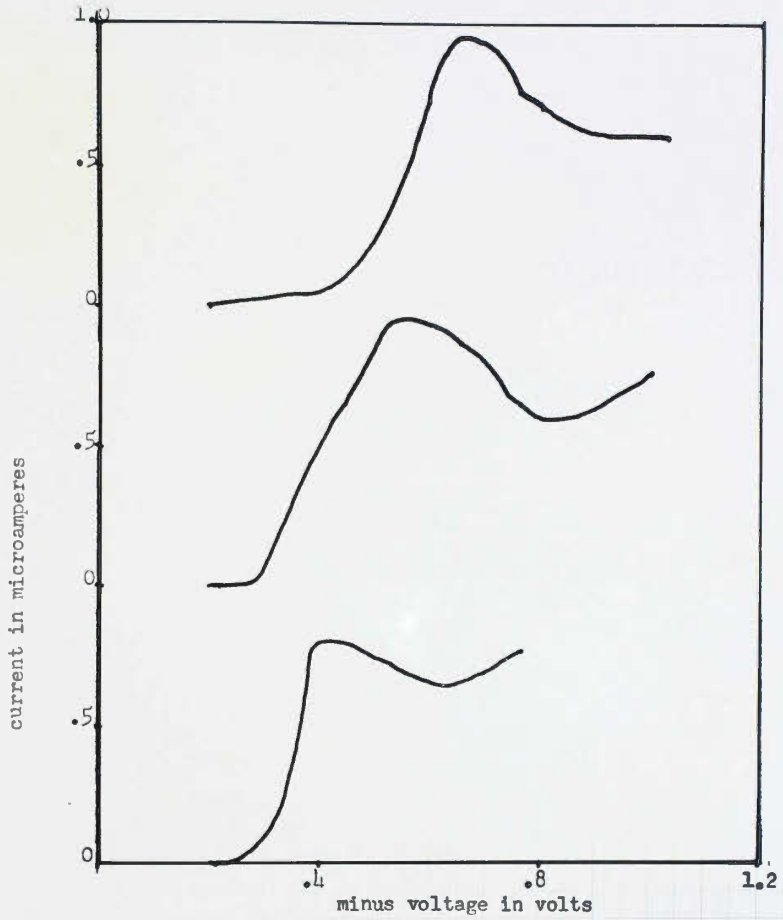

FIGURE 3
Effect of pH on Sulfur Curves

EXPERIMENTAL

Apparatus and Reagents

In polarographic determination of elemental sulfur in crude oils, the analyst is hampered by the low solubility of the crude oil in the supporting electrolyte. Hall's procedure (4) specifies a supporting electrolyte consisting of 90% methanol, 9.5% pyridine, and 0.5% concentrated hydrochloric acid. This composition was tried and was found to be an unsatisfactory solvent for crude oils. Carbon tetrachloride and dioxane were also tried and found to be unsatisfactory. The electrolyte tried and finally found to be satisfactory was that used by Eccleston (2), consisting of 63.0% benzene, 27.0% methanol, 9.5% pyridine, and 0.5% concentrated hydrochloric acid.

For the work done here, a Sargent Model XII polarograph was used with a dropping mercury electrode. A mercury-pool cell was used in the initial work, and the results were fairly satisfactory; however, there was evidence of blackening of the mercury surface. Therefore, the conventional H-type cell was used in conjunction with the saturated calomel half-cell. The calomel half-cell was the usual saturated calomel electrode, with the exception the 0.1N lithium chloride was used as the electrolyte and in the preparation of the agar plug.

Reagent grade chemicals were used in the preparation of the electrolyte solvent. Weighed amounts of powdered monoclinic sulfur dissolved in the electrolyte were used as the standard solutions. The monoclinic form was found to dissolve better than the rhombic.

The Fisher Titrimeter was used to measure the pH of the electrolyte which was found to be 6.7. The pH of the individual crude oil samples was not measured each time because they were buffered to a pH of about 7.

Procedure

For the unknown solutions, 3% solutions of crude oil were used, being diluted in 50 milliliter volumetric flasks. The amount used in the cell was 20 milliliters. Nitrogen was bubbled through the solution for 10 minutes and two trials were run on each sample, with fresh solutions being used in each case. The polarogram was obtained by using a span of -1.2 volts with a damping factor of 20. With high concentrations of elemental sulfur present, the capillary tends to become fouled and clogged up. This difficulty can be overcome by dipping the capillary in concentrated nitric acid for 2 or 3 minutes between each test run. It is then washed thoroughly with distilled water and stored in a test tube containing alcohol.

Several points in the procedure require careful attention. The elemental sulfur content of samples decreases markedly with time in solution of the electrolyte solvent. Any handling of the oil, therefore, must be done so as to reduce the time of contact to a minimum. Dissolved oxygen needs to be removed completely or it will interfere with the polarogram.

Data and Results

Calibration curves of diffusion current vs. concentration of elemental sulfur were determined with the H-type polarographic cell. A concentration of 53 parts per million of sulfur was used in the determination of the calibration. The sulfur was dissolved in the electrolyte-solvent and then a polarogram was obtained using a span e.m.f. of -1.2 volts with a damping factor of 20. This curve is shown in Figure 4. The diffusion current from this curve was then plotted against the concentration. As was mentioned before, concentration is directly proportional to diffusion current. This plot is shown in Figure 5. The half-wave potential of the sulfur curve was measured to be -0.65 volts.

The concentration of sulfur measured decreased after the electrolyte-solvent had been in contact with the sulfur for one hour. After three days there was no indication of elemental sulfur present.

The description of the crude oil samples is given in Table I.

The polarogram of the electrolyte-solvent is shown in Figure 6. The characteristic curves of the crude oil samples are given in Figures 7 thru 16. There seem to be three types of polarograms: (a) a definite rise in current after the sulfur wave had leveled off; (b) an unidentified wave at approximately -0.35 volts; and (c) a drop in current after the sulfur wave had leveled off. In the first type, the rise in current is believed to be due to the diphenyl disulfide

wave; however, this is stated without proof as the wave was not further investigated. The drop of current in the second type was also characteristic of the known standard. It was at first believed to have been due to a basic medium but upon measurement of the pH, this was not the case. Hall (4) also reports the unidentified wave produced in the third type and this was not investigated either. Only one sample, Law Lansing Pool, showed no indication of sulfur.

A correlation between sulfur content and type of formation was anticipated but none was found whatsoever, as can be seen from Table II. The results are in good agreement except for those of the Happy Pool (Ninemire #1). The reason for this change in concentration is not known.

The current and voltage for each sample are given in Tables III and IV, which are representative of the trials run.

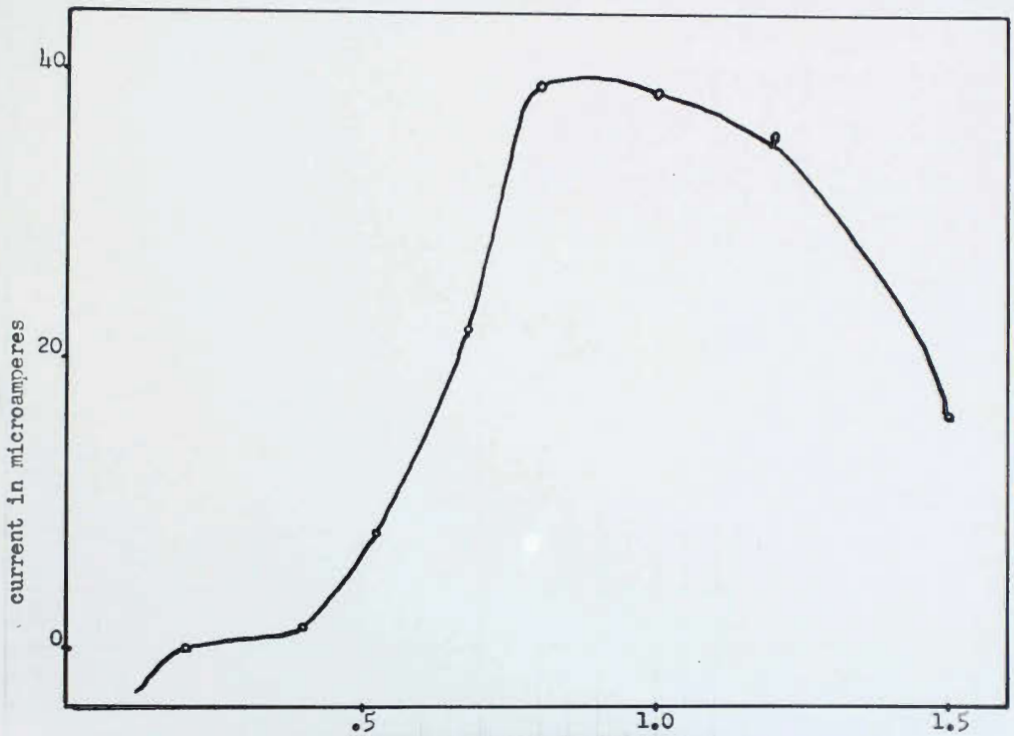

FIGURE 4
Polarogram of Known Elemental Sulfur
Content in Electrolyte-Solvent

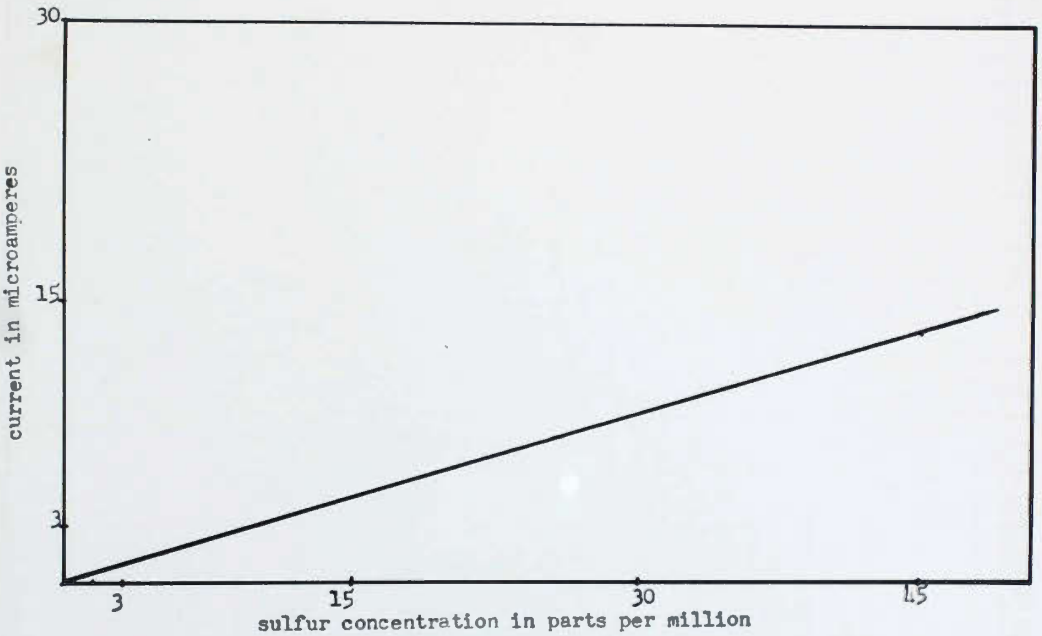

FIGURE 5
Sulfur Concentration vs. Diffusion Current

TABLE I

ORIGIN OF SAMPLES

	County	Pool	Lease	Formation
1.	Rooks	Irwin	Irwin #3	Arbuckle
2.	Trego	Happy	Ninemire #1	Kansas City
3.	Trego	Happy	Stewart #1	Kansas City
4.	Ellis	Brock	Brock	Arbuckle
5.	Barton	Harris	Morgenstern #2	Arbuckle
6.	Barton	Harris	Morgenstern #3	Arbuckle
7.	Graham	Holly Lansing	#7	Kansas City
8.	Graham	Law Lansing	#6	Kansas City
9.	Trego	Sunny Slope	Wicks	Arbuckle
10.	Rooks	Kern	Kern	Arbuckle

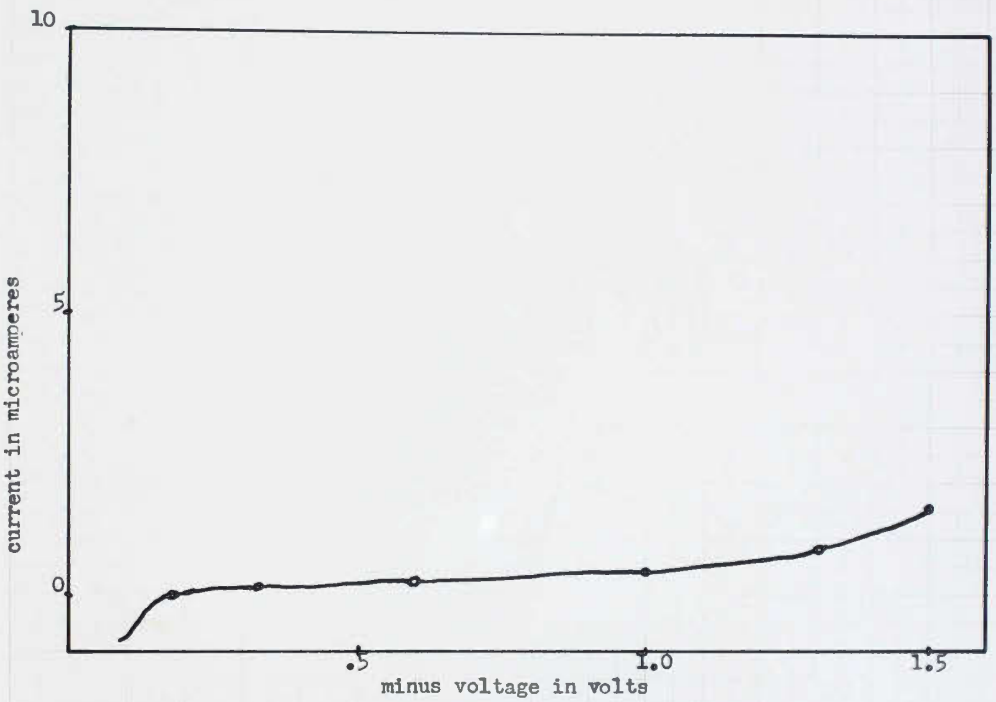

FIGURE 6
Polarogram of Electrolyte-Solvent

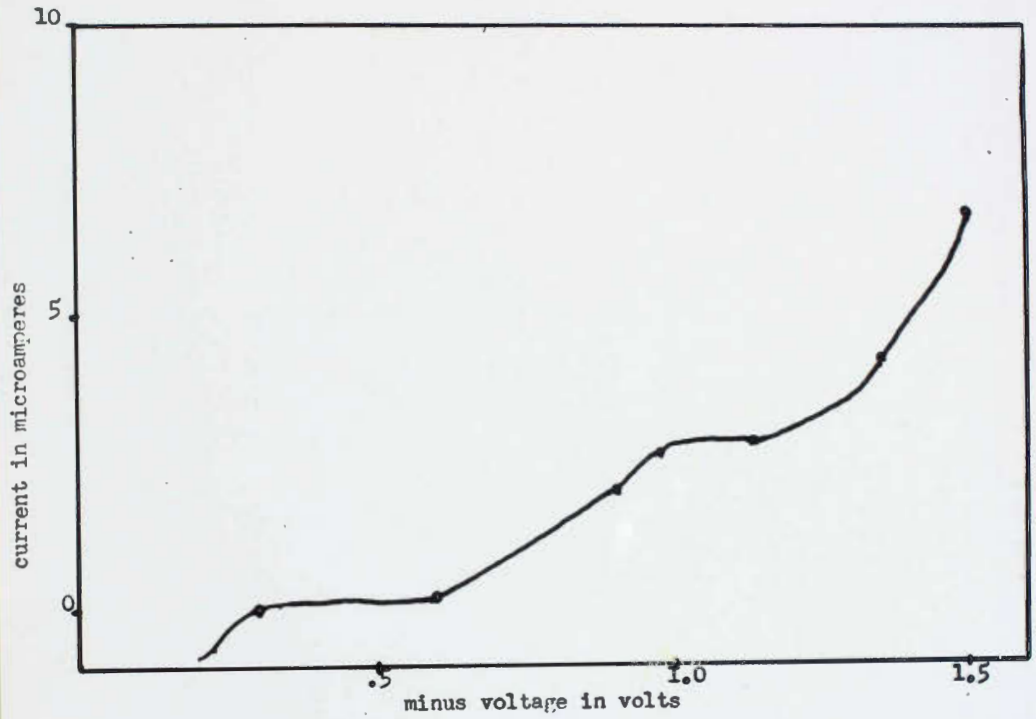

FIGURE 7
Polarogram of Elemental Sulfur
from the Irwin Pool

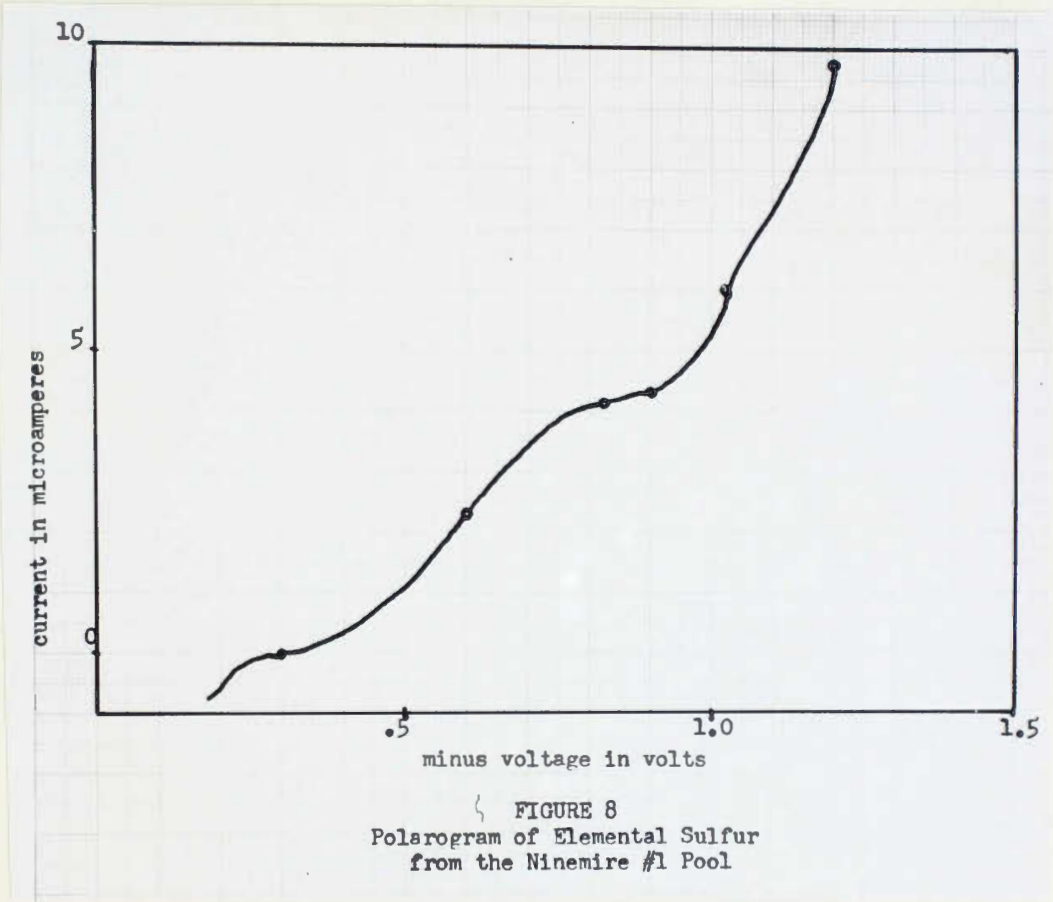

FIGURE 8
Polarogram of Elemental Sulfur
from the Ninemire #1 Pool

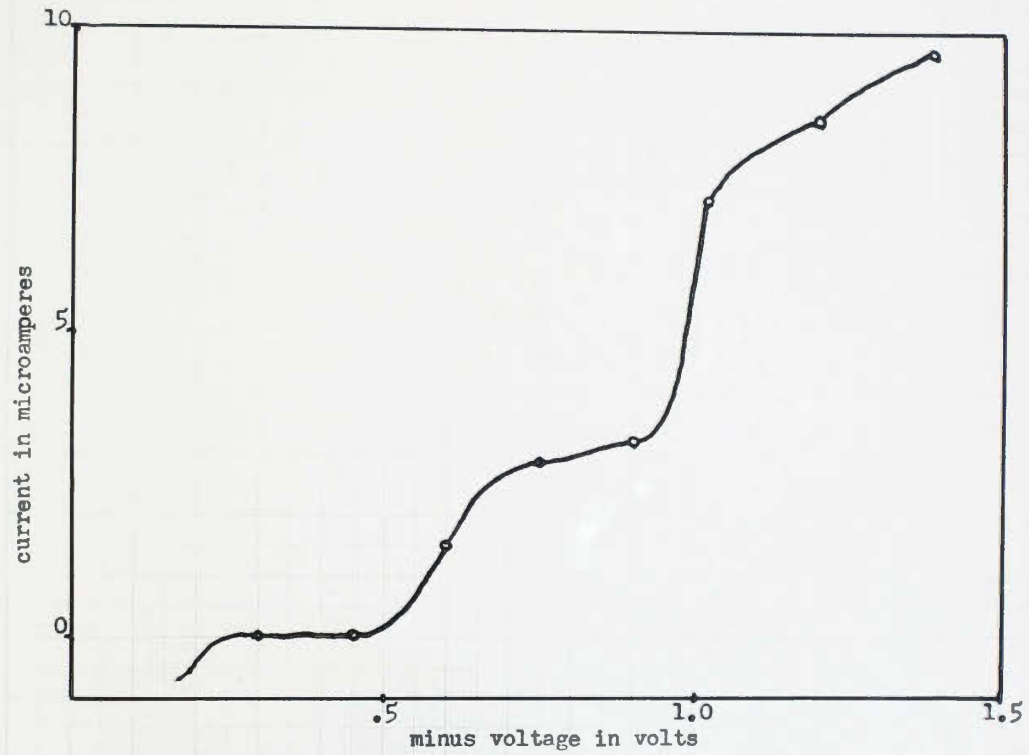

FIGURE 9
Polarogram of Elemental Sulfur
from the Holly Lansing Pool

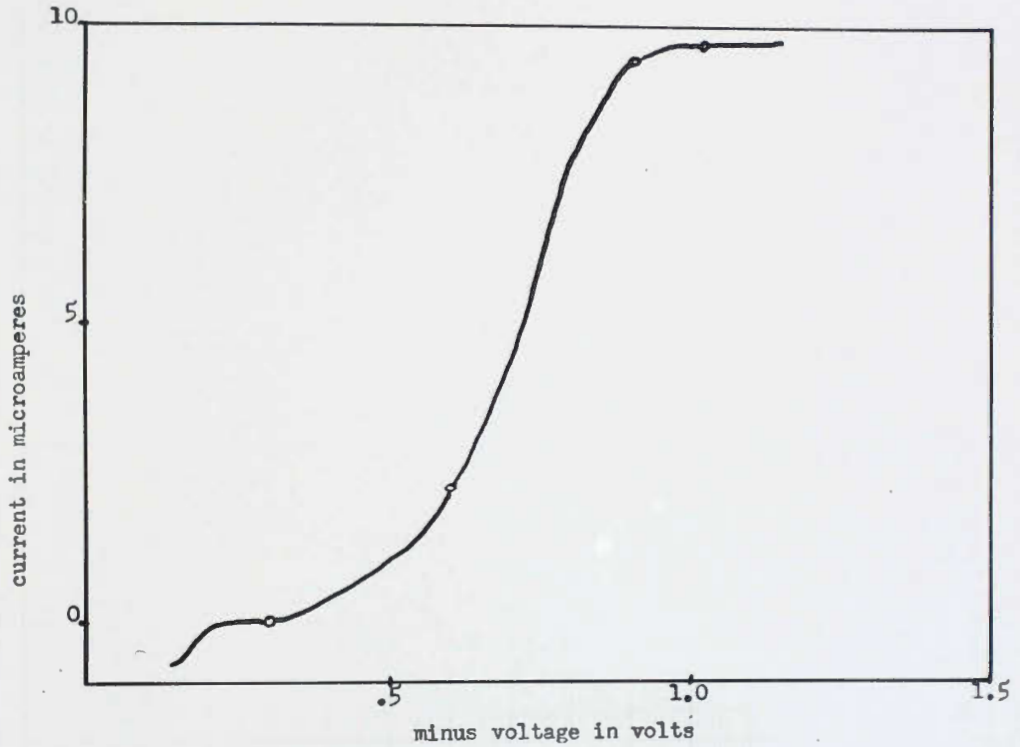

FIGURE 10
Polarogram of Elemental Sulfur
from the Sunny Slope Pool

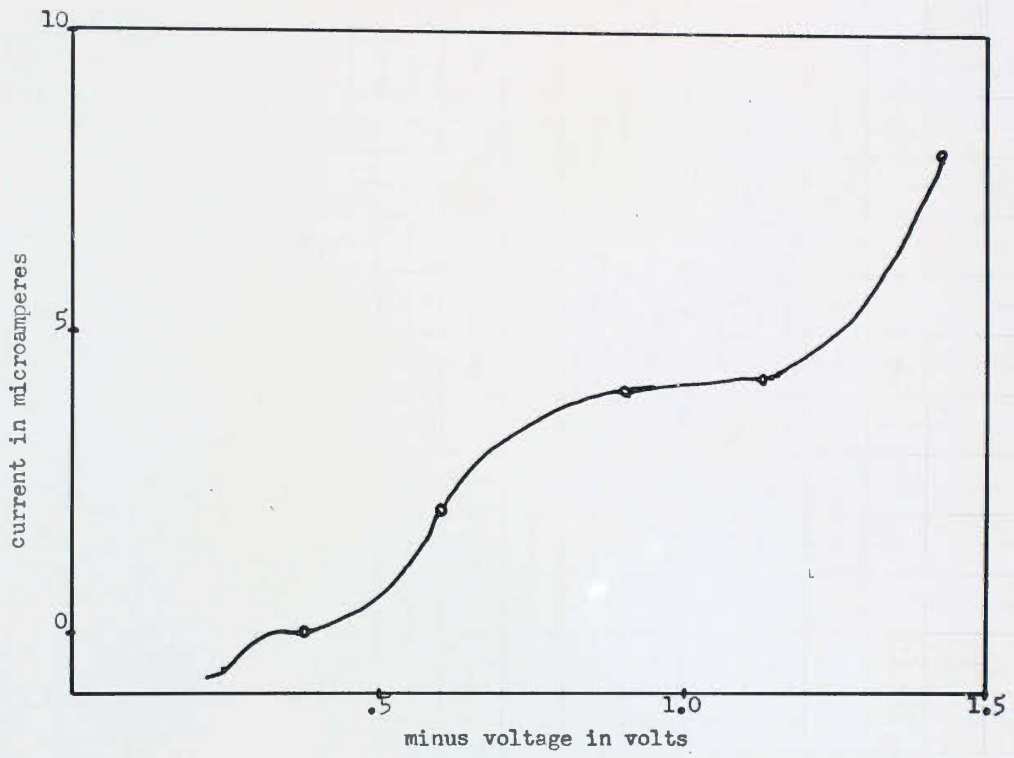

FIGURE 11
Polarogram of Elemental Sulfur
from the Brook Pool

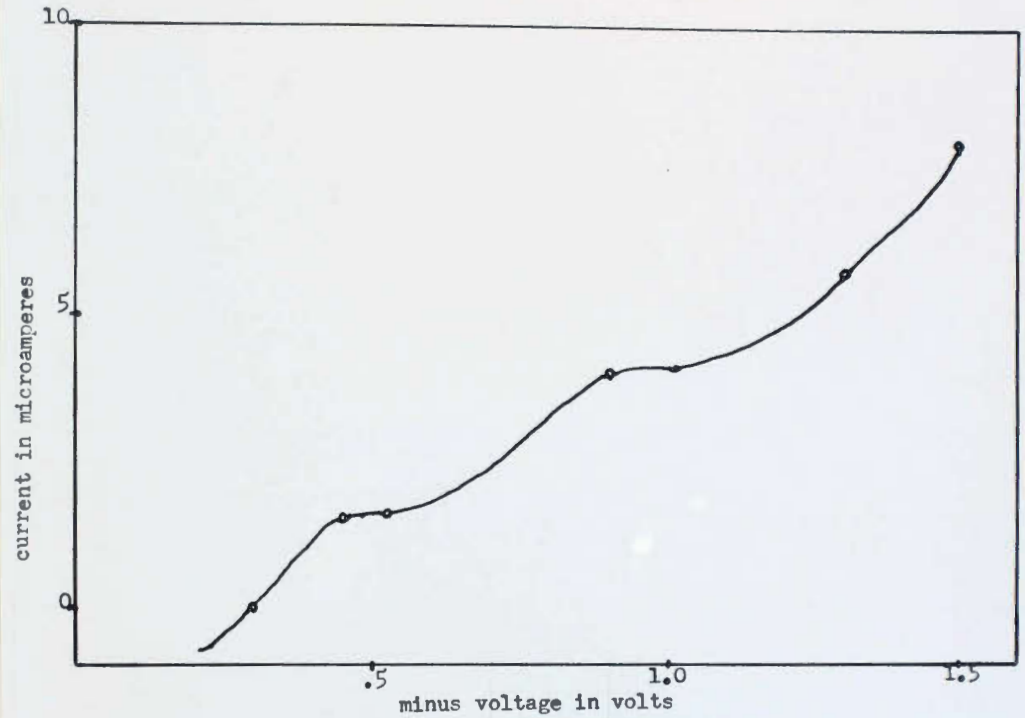

FIGURE 12
Polarogram of Elemental Sulfur
from the Kern Pool

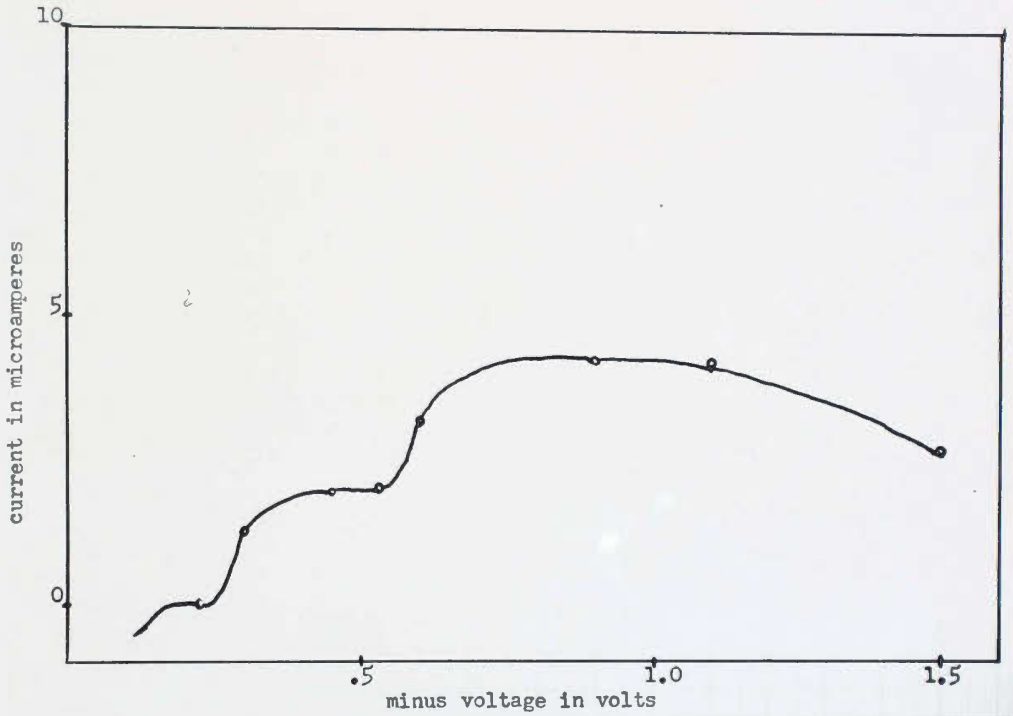

FIGURE 13
Polarogram of Elemental Sulfur
from the Harris #3 Pool

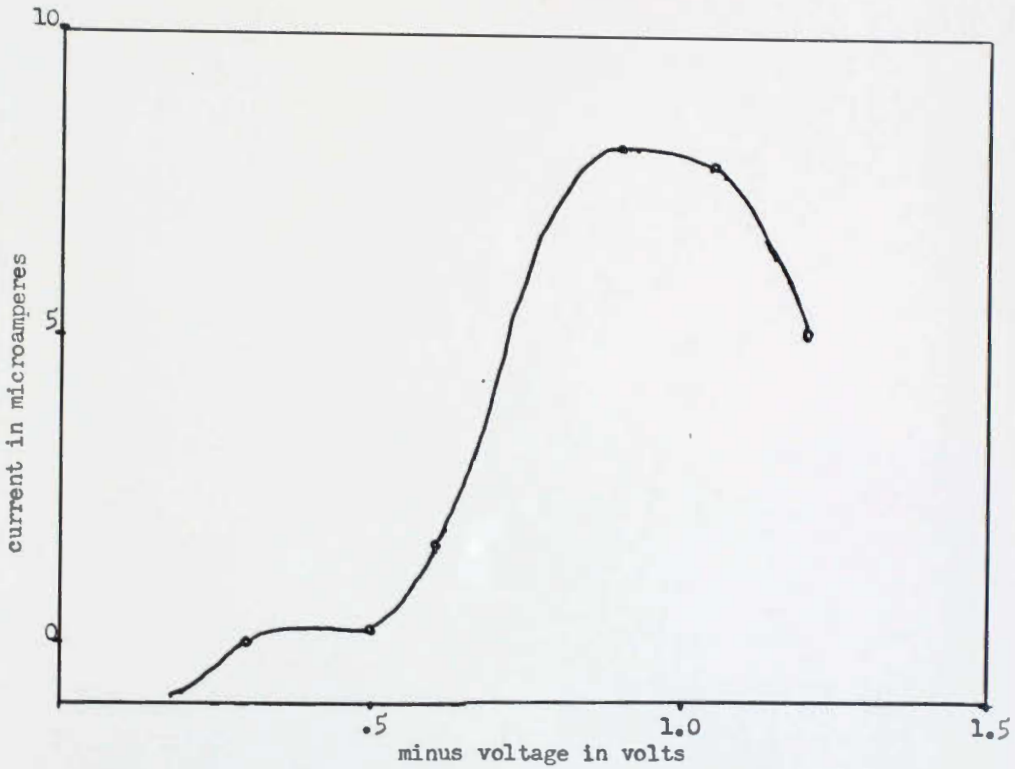

FIGURE 14
Polarogram of Elemental Sulfur
from the Harris #2 Pool

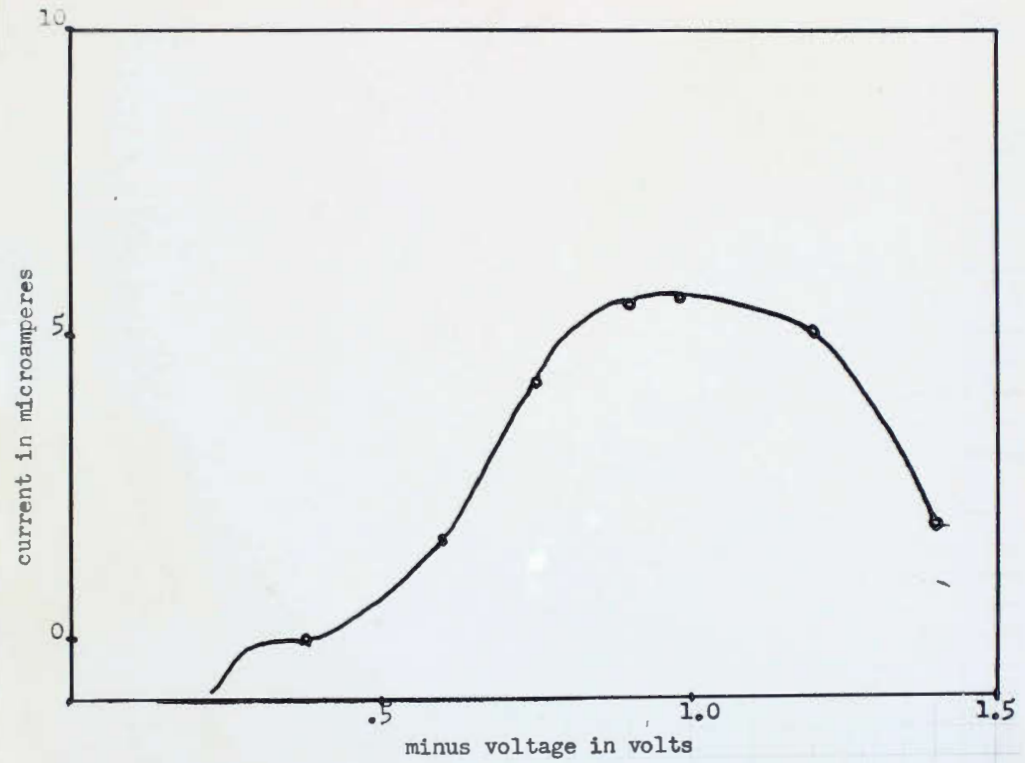

FIGURE 15
Polarogram of Elemental Sulfur
from the Stewart #1 Pool

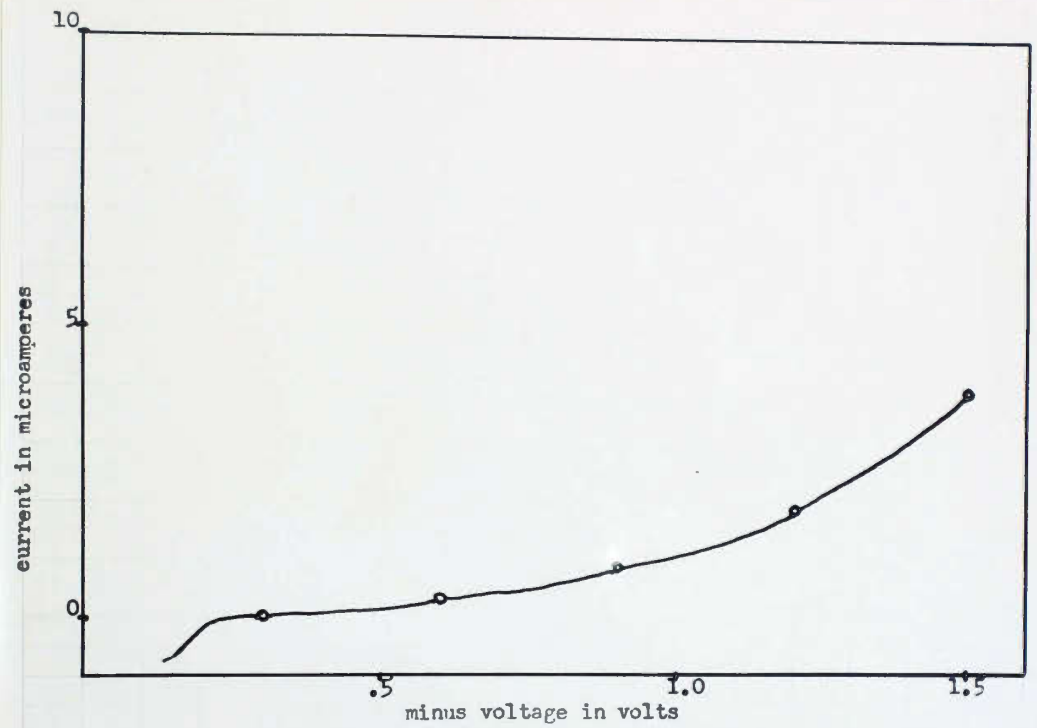

FIGURE 16
Polarogram of Elemental Sulfur
from the Law Lansing Pool

TABLE II

SULFUR CONCENTRATION, HALF WAVE

POTENTIAL AND DIFFUSION CURRENT

Pool	Sulfur (p.p.m.) Electrolyte	Crude Oil	$E_{\frac{1}{2}}$ (v)	i_d (a)
Irwin	8.2	273.0	-0.60	2.64
	8.0	266.4	.62	2.40
Happy (Ninemire)	2.6	86.6	.65	1.00
	16.8	559.4	.65	5.20
Happy (Stewart)	14.0	466.2	.61	4.12
	13.7	455.2	.65	4.00
Brock	12.3	409.6	.64	3.80
	12.6	419.6	.66	3.96
Harris #2	20.9	696.0	.66	6.20
	20.4	679.3	.60	6.00
Harris #3	8.9	296.4	.64	2.74
	9.0	299.7	.63	2.76
Holly Lansing	7.3	243.1	.61	2.50
	6.8	226.4	.64	2.00
Law Lansing	0	0	0	0
	0	0	0	0
Sunny Slope	29.4	979.0	.61	8.74
	29.8	992.3	.63	8.80
Kern	6.0	199.8	.60	2.16
	11.0	396.3	.64	3.30

TABLE III

CURRENT VOLTAGE RELATIONSHIPS

-E (v.)	i(μa) Irwin	Ninemire	Stewart	Brock	Harris #2
0	0	0	0	0	0
.075	-5.00	-6.00	-4.00	-.80	-2.00
.150	1.75	4.00	1.60	1.20	1.20
.225	0	1.80	.40	.20	.30
.300	0	0	.20	.07	0
.375	+.10	+.30	0	0	0
.450	.15	.60	+.01	+.01	+1.10
.525	.30	1.70	.14	.95	1.50
.600	.40	2.30	1.60	2.00	1.60
.675	.64	3.90	2.50	2.50	3.50
.750	1.10	4.10	4.20	3.00	5.60
.825	1.50	4.20	5.45	3.75	6.00
.900	2.00	4.30	5.50	4.00	8.15
.975	2.60	5.00	5.60	4.15	8.00
1.05	2.62	6.00	5.60	4.20	7.50
1.125	2.64	7.00	5.55	4.50	5.00
1.200	3.80	9.00	4.15	5.00	3.20
1.275	5.00	10.10	3.20	6.00	2.05
1.350	5.80	11.45	2.00	7.00	1.15
1.425	6.00	12.00	1.55	8.00	1.00
1.500	6.80	13.14	1.00	9.10	1.00

TABLE IV

CURRENT VOLTAGE RELATIONSHIPS

-E (v.)	i(μa) Harris #3	Holly Lansing	Law Lansing	Sunny Slope	Kern
0	0	0	0	0	0
.075	-2.00	-3.00	-2.00	-3.60	-3.00
.150	1.20	2.00	.80	1.40	2.00
.225	0	.50	.30	0	.40
.300	+1.35	0	0	0	0
.375	1.90	0	0	+.20	0
.450	1.95	0	+.20	.40	+1.52
.525	2.00	+.30	.25	1.54	1.59
.600	3.15	1.50	.30	2.21	1.85
.675	3.70	2.22	.37	3.92	2.47
.750	4.15	2.95	.45	5.64	3.56
.825	4.20	3.00	.62	7.29	4.05
.900	4.20	3.25	.97	9.42	4.00
.975	4.20	5.41	1.12	9187	4.15
1.05	4.10	7.26	1.34	10.00	4.34
1.125	4.00	8.00	1.60	10.10	4.96
1.200	3.46	8.54	1.92	10.32	5.44
1.275	3.24	9.10	2.24	10.74	5.96
1.350	3.10	9.92	2.54	11.26	6.50
1.425	3.00	10.11	3.14	11.82	7.25
1.500	2.60	10.94	3.90	12.00	8.00

CONCLUSION

For the polarographic analysis of elemental sulfur in crude oil a mixture of benzene, methanol, pyridine and concentrated hydrochloric acid proved to be a satisfactory electrolyte-solvent. The pH of the solvent is not too critical as long as it is less than 7. Buffers should be used since the half-wave potential shifts with pH. Diphenyl disulfide will interfere in the analysis of elemental sulfur since the two substances have approximately the same half-wave potentials in acid media.

The data presented confirm the presence of elemental sulfur in some Central Kansas crude oils. The samples were taken as near as conveniently possible to their source in the earth, but the possibility of change in elemental sulfur content between wellhead and bottom hole has not been investigated. The data also demonstrate that the polarographic method for elemental sulfur can be applied satisfactorily to Kansas crude oil. However, some precautions must be taken, mainly: (a) analyzing the crude oil as soon as possible after it comes into contact with the electrolyte; (b) efficient sweeping of dissolved oxygen; (c) pH value and presence of a buffer; and (d) a preventive measure taken to decrease "souring" of the oil.

BIBLIOGRAPHY

1. Daniels, Farrington, and staff, Experiment 38 in Experimental Physical Chemistry, (New York, McGraw-Hill Book Co., 4th ed. 1949.

2. Eccleston, B. H., Marilyn Morrison and H. M. Smith, "Elemental Sulfur in Crude Oil, " Analytical Chemistry, (Easton, Penn., American Chemical Society, 1952) Vol. 24, pp. 1745-48.

3. Gerber, M. I., Journal of Analytical Chemistry, (U. S. S. R.), 1950, Vol. 5, p. 262.

4. Hall, Maynard E., "Polarographic Determination of Elemental Sulfur in Petroleum Fractions, "Analytical Chemistry, (Easton, Penn., American Chemical Society, 1950) Vol. 22, pp. 1137-39.

5. Hall, Maynard E., "Polarographic Studies of Sulfur Compounds in Petroleum Fractions, "Analytical Chemistry, (Easton, Penn., American Chemical Society, 1953) Vol. 25, pp. 556-61.

6. Kolthoff, I. M. and James Lingane, Polarography, (New York, Interscience Publishers, 2nd ed., 1952) Vol. I and II.

7. Kolthoff, I. M. and James Lingane, "Fundamental Studies with the Dropping Mercury Electrode. I. Ilkovic Equation of Polarographic Diffusion Currents," Journal of American Chemical Society, (Easton, Penn., American Chemical Society, 1939) Vol. 61, pp. 825-834.

8. Kolthoff, I. M. and James Lingane, "Fundamental Studies with the Dropping Mercury Electrode. II. The Migration Current", Journal of American Chemical Society, (Easton, Penn., American Chemical Society, 1939) Vol. 61, pp. 1045-51.

9. Kolthoff, I. M. and James Lingane, "Polarographic Method of Chemical Analysis," Chemical Reviews, (Baltimore, Williams and Wilkins Co., 1939) Vol. 24, pp. 1-95.

10. Kolthoff, I. M. and E. F. Orlemann, "Elimination of the Water Wave in Polarographic Work," Industrial and Engineering Chemistry, Analytical Edition, (Easton, Penn., American Chemical Society, 1942) Vol. 14, pp. 321-23.

11. Lingane, James, "Polarographic Theory, Instrumentation, and Methodology," Analytical Chemistry, (Easton, Penn., American Chemical Society, 1949) Vol. 21, pp. 45-60.

12. Lingane, James, "Influence of External Resistance in the Cell Circuit on the Maxima in Polarographic Current-Voltage Curves," Journal of American Chemical Society, (Easton, Penn., American Chemical Society, 1940) Vol. 62, pp. 1665-67.

13. Lingane James and Brian Loveridge, "Fundamental Studies with the Dropping Mercury Electrode. III. Influence of Capillary Characteristics on the Diffusion Current and Residual Current," Journal of American Chemical Society, (Easton, Penn., American Chemical Society, 1944) Vol. 66, pp. 1425-31.

14. Lingane James and Brian Loveridge, "Fundamental Studies with the Dropping Mercury Electrode. IV. Empirical Modification of the Ilkovic Equation," Journal of American Chemical Society, (Easton, Penn., American Chemical Society, 1946) Vol. 68, pp. 395-7.

15. Lingane, James and Brian Loveridge, "A New Polarographic Diffusion Current Equation," Journal of American Chemical Society, (Easton, Penn., American Chemical Society, 1950) Vol. 72, pp. 438-41.

16. Muller, Otto, "Research with the Polarograph," Industrial and Engineering Chemistry, Analytical Edition, (Easton, Penn., American Chemical Society, 1942) Vol. 14, pp. 99-104.

17. Muller, Otto, Chapter XXVIII in Physical Methods of Organic Chemistry, (New York, Interscience Publishers, Inc., A. Weissberger, editor, 1949) Vol. I.

18. Proske, G., Angew. Chem. (1947) Vol. A59, p.121.

19. Willard, Hobart, Lynne Merritt and John Dean, Instrumental Methods of Analysis, (New York, D. Van Nostrand Co., 2nd ed., 1951) pp. 263-5.